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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁶ : C08F 220/04, A61K 7/00	A1	(11) International Publication Number: WO 99/65958 (43) International Publication Date: 23 December 1999 (23.12.99)
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(54) Title: ALKALI SOLUBLE LATEX THICKENERS		
(57) Abstract Alkali soluble thickeners are disclosed which comprise a reaction product of (A) an unsaturated carboxylic acid monomer, (B) a monoethylenically unsaturated monomer different from monomer (A), and (C) a hydrophobic, alkoxylated macromonomer polymerizable with monomers (A) and (B). The monoethylenically unsaturated monomer different from monomer (A) comprises a methyl group, preferably is an acrylate and more preferably is methyl acrylate. The polymers disclosed solubilize at a pH of from about 4.5 to 6.0, thereby rendering the polymers particularly suitable for use in cosmetic compositions.		

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ALKALI SOLUBLE LATEX THICKENERS

Field of the Invention

The present invention relates to latex polymers which are alkali soluble and more specifically to latex polymers which demonstrate viscosity enhancement at a pH of less than about 6.

Background of the Invention

As used herein, the term "alkali soluble thickeners" means latex polymers which become soluble in aqueous medium upon the addition of a sufficient amount of a base to raise the pH to a level effective to cause the latex polymer to become soluble in the aqueous medium.

Alkali soluble thickeners have found great acceptance in industrial applications, such as, for example, use in coating compositions, e.g., latex paints. Such alkali soluble thickeners are disclosed for example in U.S. Patent Nos. 4,514,552, issued April 30, 1985; 4,722,962 issued February 2, 1988 and 5,292,828 issued March 8, 1994. Such alkali soluble thickeners typically comprise the aqueous emulsion reaction product of (A) a monoethylenically unsaturated carboxylic acid, e.g., methacrylic acid, (B) a monoethylenically unsaturated monomer different from monomer (A), e.g. ethyl acrylate and (C) a macromonomer comprising a hydrophobic portion and an alkoxyated portion which is polymerizable with monomer (A) and monomer (B). Often, the macromonomer is a urethane monomer which is the urethane reaction product of a monohydric surfactant and a monoethylenically unsaturated monoisocyanate. Typically, the

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monohydric surfactant comprises an ethyloxated or propoxylated aliphatic alcohol or alkyl phenol.

Typically, alkali soluble thickeners such as described above begin to solubilize and demonstrate viscosity enhancement at a pH of greater than 6.0 and often in the range of about 6.5 or higher. The maximum viscosity is often not achieved until a pH of 7.5 or higher is reached. Accordingly, such alkali soluble thickeners have not found wide acceptance in personal care applications, e.g., hair care and skin care compositions, since personal care compositions typically require significant viscosity enhancement at or below the pH of skin, e.g. from about 6.5 to 6.8.

Accordingly, improved alkali soluble thickeners are desired which can demonstrate viscosity enhancement at a pH of less than about 6.0.

Summary of the Invention

By the present invention, it is now possible to provide alkali soluble latex polymers which are suitable for use in personal care applications, e.g., hair care compositions and skin care compositions. The polymers of the present invention comprise the reaction product of (A) an unsaturated carboxylic acid monomer, (B) a monoethylenically unsaturated monomer different from (A), and (C) a macromonomer comprising a hydrophobic portion and an alkoxyated portion which is polymerizable with monomer (A) and monomer (B). Quite surprisingly, in accordance with the present invention, it has

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been found that when the monoethylenically unsaturated monomer (B) comprises a methyl group, preferably methyl acrylate, solubilization of the polymer occurs at a pH of from about 4.5 to 6, thereby making the polymer suitable for use in personal care applications. In addition, it has been found quite surprisingly in accordance with the present invention that the utilization of a long chain aliphatic alcohol in the preparation of the macromonomer can yield a polymer having desirable shear thinning properties.

Detailed Description of the Invention

The unsaturated carboxylic acid monomers suitable for use in accordance with the present invention are typically α,β -monethylenically unsaturated carboxylic acids. Preferred carboxylic acid monomers are selected from the group consisting of acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, and mixtures thereof. Methacrylic acid is especially preferred. The concentration of the carboxylic acid monomer is typically from about 20 to 70 weight percent, preferably from about 20 to 50 weight percent and more preferably from about 35 to 45 weight percent based on the total weight of the polymer. The amount of the carboxylic acid monomer is preferably sufficient to provide a polymeric structure which will solubilize and provide viscosity enhancement when reacted with an alkali such as for example, sodium hydroxide.

In accordance with the present invention, the monoethylenically unsaturated monomer different from

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monomer (A) is one which comprises a methyl group. Preferably, this monomer is an acrylate. More preferably, this monomer is methyl acrylate. Typically, the amount of the monoethylenically unsaturated monomer different from monomer (A) is from about 20 to 80 weight percent, preferably from about 30 to 65 weight percent and more preferably from about 45 to 55 weight percent based on the total weight of the polymer.

The macromonomers suitable for use in accordance with the present invention comprise a hydrophobic portion, an alkoxyated portion and which is polymerizable with monomer (A) and monomer (B). As used herein, the term "macromonomer" means a polymerizable monomer which comprises the reaction product of two or more compounds. Such macromonomers include, for example, any alkoxyated, e.g., ethoxyated or propoxyated, monomers having ethylenic unsaturation and which are terminated by a hydrophobic fatty chain. Examples of unsaturated, polymerizable moieties include those selected from the group consisting of vinyl group containing moieties, methacryloyl, maleoyl, itaconoyl, crotonyl, an unsaturated urethane moiety, hemiester maleoyl, hemiester itaconoyl, $\text{CH}_2=\text{CHCH}_2\text{-O-}$, methacrylamido and substituted methacrylamido. Examples of hydrophobic moieties include those selected from the group consisting of alkyl, alkaryl, i.e., alkylaryl or aralkyl, or aryl, linear or branched, saturated or unsaturated, and having at least 6 carbon atoms, preferably from about 6 to 30 carbon atoms per molecule.

Preferred macromonomers are urethane monomers which comprise the reaction product of a monohydric surfactant and a monoethylenically unsaturated isocyanate. Preferably the urethane monomer is a nonionic, urethane monomer which is the urethane reaction product of a monohydric, nonionic surfactant with a monoethylenically unsaturated monoisocyanate, preferably one lacking ester groups, e.g., alpha, alpha-dimethyl-m-isopropenyl benzyl isocyanate. The monohydric nonionic surfactants are themselves well known and are usually alkoxyated, e.g., ethoxyated, hydrophobes containing adducted ethylene oxide to provide the hydrophilic portion of the molecule. The hydrophobes are usually aliphatic alcohols or alkyl phenols in which a carbon chain containing at least 6 carbon atoms, preferably about 6 to 30 carbon atoms, provides the hydrophobic portion of the surfactant. These surfactants are illustrated by ethylene oxide adducts of dodecyl alcohol or octyl or nonyl phenol which are available in commerce and which contain about 5 to about 150, preferably 25 to 60 moles of ethylene oxide per mole of hydrophobe. Other hydrophobic substituents, such as complex hydrophobes, disclosed for example in U.S. Patent 5,488,180 issued January 30, 1996, are suitable for use in accordance with the present invention.

In a preferred aspect of the invention, the hydrophobic portion of the surfactant comprises an aliphatic alcohol containing from about 20 to 24 carbon atoms. More preferably the aliphatic alcohol is of a vegetable origin. Even more preferably, the aliphatic alcohol is behenyl alcohol.

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The monoethylenically unsaturated isocyanates suitable for use in preparing the urethane monomers can be any isocyanates effective to form the desired urethane linkage. Preferably, the isocyanate is a monoethylenically unsaturated monoisocyanate. Any copolymerizable unsaturation may be employed, such as acrylate and methacrylate unsaturation. One may also use allylic unsaturation, as provided by allyl alcohol. These, preferably in the form of a hydroxy-functional derivative, as is obtained by reacting a C₂-C₄ monoepoxide, like ethylene oxide, propylene oxide or butylene oxide, with acrylic or methacrylic acid to form an hydroxy ester, are preferably reacted in equimolar proportions with an organic diisocyanate, such as toluene diisocyanate or isophorone diisocyanate. The preferred monoethylenic monoisocyanate is styryl, as in alpha, alpha-dimethyl-m-isopropenyl benzyl isocyanate, and this unsaturated monoisocyanate lacks the ester group so it forms urethanes which lack this group. The amount of the monoethylenically unsaturated isocyanate relative to the monohydric surfactant used in making the macromonomer, (on a mole ratio basis) is typically from about 0.1-2.0 to 1, preferably about 1.0 to 1.0.

Typically, the amount of monomer (C) is from about 0.5 to 60 weight percent, preferably from about 5 to 50 weight percent and more preferably from about 5 to 15 weight percent based on the total weight of the polymer. Typically, the molecular weight of the macromonomers ranges from about 400 to 8000 grams per gram mole. As used herein, the term "molecular weight" means weight average molecular weight. Techniques for measuring weight average molecular weight are known to those skilled in

the art. One such technique, is gel permeation chromatography. Further details concerning the preparation of such macromonomers are known to those skilled in the art and are disclosed for example in U.S. Patent Nos. 4,514,552, 4,801,671, 5,292,828 and 5,294,693.

In addition to the specific monomers described above, additional monomers can be utilized in preparing the polymers of the present invention. For instance, a polyethylenically unsaturated monomer may be copolymerized into the polymer, as is common in alkali soluble emulsion copolymers. These are illustrated by ethylene glycol diacrylate or dimethacrylate 1,6-hexanediol diacrylate or dimethylacrylate, divinyl benzene, and the like. Further details concerning such additional monomers and other monomers suitable for copolymerization in accordance with the present invention are known to those skilled in the art. Such additional monomers typically comprise from 0 to about 10 weight percent based on the total weight of the polymer.

One or more of each class of monomers described above can be used in preparing the polymers of the present invention. Furthermore, in addition to the specific monomers within each class, those skilled in the art will recognize that other monomers within such classes may be utilized in accordance with the present invention. Such monomers are generally commercially available.

The latex polymers of the present invention are prepared in colloidal form, i.e., aqueous dispersions, and can be prepared by emulsion polymerization in the presence of a chain transfer agent and an initiator. Specific details concerning procedures

and conditions for emulsion polymerization are known to those skilled in the art. See, for example, U.S. Patent 5,629,375 issued May 13, 1997. Typically, however, the polymerization is carried out in an aqueous medium at a temperature of from about 35 to 90°C. The pressure is not critical and is dependent upon the nature of the monomers employed.

Chain transfer agents are normally not used in the polymerization. However, if chain transfer agents are employed, they are typically present during the polymerization reaction at a concentration of from about 0.01 to 5 weight percent, preferably from about 0.1 to 1 weight percent based on the total monomer content. Both water-insoluble and water-soluble chain transfer agents can be employed. Illustrative of substantially water-soluble chain transfer agents are alkyl and aryl mercaptans such as butyl mercaptan, mercaptoacetic acid, mercaptoethanol, 3-mercaptol-1,2-propanediol and 2-methyl-2-propanethiol. Illustrative of the substantially water-insoluble chain transfer agents include, for example, t-dodecyl mercaptan, phenyl mercaptan, pentaerythritol tetramercaptopropionate, octyldecyl mercaptan, tetradecyl mercaptan and 2-ethylhexyl-3-mercaptopropionate.

In carrying out the emulsion polymerization an initiator is preferably used at a concentration sufficient to initiate the polymerization reaction. This will typically vary from about 0.01 to 3 weight percent based on the weight of monomers charged. However, the concentration of initiator is preferably from about 0.05 to 2 weight percent and, most preferably, from about 0.1 to 1 weight percent of the monomers charged. The particular

concentration used in any instance will depend upon the specific monomer mixture undergoing reaction and the specific initiator employed, which details are known to those skilled in the art. Illustrative of suitable initiators include hydrogen peroxide, peracetic acid, t-butyl hydroperoxide, di-t-butyl hydroperoxide, dibenzoyl peroxide, benzoyl hydroperoxide, 2,4-dichlorobenzoyl peroxide, 2,5-dimethyl-2,5-bis(hydroperoxy) hexane, perbenzoic acid, t-butyl peroxyphthalate, t-butyl peracetate, dilauroyl peroxide, dicapryloyl peroxide, distearoyl peroxide, dibenzoyl peroxide, diisopropyl peroxydicarbonate, didecyl peroxydicarbonate, dicosyl peroxydicarbonate, di-t-butyl perbenzoate, 2,2'-azobis-2,4-dimethylvaleronitrile, ammonium persulfate, potassium persulfate, sodium persulfate, sodium perphosphate, azobisisobutyronitrile, as well as any of the other known initiators. Also useful are the redox catalyst systems such as sodium persulfate-sodium formaldehyde sulfoxylate, t-butyl hydroperoxide - isoascorbic acid, , t-butyl hydroperoxide-sodium persulfate-sodium formaldehyde sulfoxylate, cumene hydroperoxide-sodium metabisulfite, hydrogen peroxide-ascorbic acid, and other known redox systems. Moreover, as known by those skilled in the art, traces of metal ions can be added as activators to improve the rate of polymerization, if desired.

The particular surfactant useful for conducting the polymerization reaction is not critical to the present invention. Typical surfactants include anionic surfactants such as sodium lauryl sulfate, sodium tridecylether sulfate, diester sulfosuccinates and sodium salts of alkyl aryl polyether sulfonates; and nonionic surfactants such as alkyl aryl polyether

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alcohols and ethylene oxide condensates of propylene oxide, propylene glycol adducts. Preferably, the initiators and surfactants are selected to minimize the odor of the final product.

The reaction products comprising the latex polymers of the present invention typically have a solids, i.e. polymer, content of from about 10 to 65 weight percent, preferably from about 20 to 50 weight percent based on the weight of the latex and water. Typically, the particle size of the latex polymer is from about 0.1 to 1.0 microns. The Tg of the latex polymers of the present invention is typically from about 20 to 60 C. As used herein, the term "Tg" means polymer glass transition temperature. Techniques for measuring the glass transition temperature of polymers are known to those skilled in the art. One such technique is, for example, differential scanning calorimetry. A particularly useful means of estimating the glass transition temperature of a polymer is that given Fox,

$$1/T_{g(\text{polymer})} = x_1/T_{g1} + x_2/T_{g2} + x_3/T_{g3} + \dots + x_n/T_{gn} \quad (1)$$

where x_i is the weight fraction of component i in the copolymer and T_{gi} is the homopolymer glass transition of component i . The homopolymer glass transition temperatures can be found in any publicly available source such as the Polymer Handbook.

Typically the viscosity of the latex polymers of the present invention is from about 5 to 1500 centipoise ("cP") in the un-neutralized form measured at 20°C with a 20 to 50 weight percent solids composition using a Brookfield Viscometer with a number 2 spindle at 60 revolutions per minute. The molecular

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weight of the latex polymers of the present invention is typically from about 10^4 to 10^7 , preferably from about 200,000 to 1,000,000 grams per gram mole.

In accordance with the present invention the latex polymers begin to become soluble in the aqueous medium at a pH of less than about 6.0, preferably at a pH of from about 4.5 to 6.0, and more preferably at a pH from about 5.0 to 6.0. Significant solubilization, i.e., 90 % of maximum viscosity, preferably occurs at a pH of about 7.5 or less, more preferably at a pH of about 7.0 or less. The solubilization is effected by the introduction of a suitable alkali, such as, for example, sodium hydroxide, potassium hydroxide, ammonium hydroxide, amines, for example, triethyl amine, and other alkali materials known to those skilled in the art. Upon the solubilization of the latex polymers, the viscosity of the aqueous medium demonstrates a significant increase. Preferably in accordance with the present invention, aqueous compositions comprising the solubilized polymers of the present invention have a viscosity of greater than about 10,000 cP, preferably greater than about 20,000 cP, more preferably greater than about 40,000 cP, and most preferably greater than about 60,000 cP at a pH of less than about 6.0. Unless otherwise stated, the viscosity measurement of the solubilized polymer is taken at a polymer concentration of 1.0 weight percent based on the total weight of the aqueous composition using a Brookfield LVT DV-II viscometer at 20°C using a No. 3 spindle at 12 rpm.

Quite surprisingly, in accordance with the present invention, it has been found that by utilizing a straight chain

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aliphatic alcohol having from about 20 to 24 carbon atoms as the hydrophobe in the manufacture of the macromonomer, the polymers of the present invention in their solubilized state have desirable shear thinning characteristics. Note the following data in Table 1 below.

TABLE 1

Spindle Speed (rpm)	Viscosity, cPs
0.3	1658550
0.6	895220
1.5	396200
3.0	213860
6.0	115430
12.0	62300
30.0	27575
60.0	14885

In general, the polymers of the present invention are particularly effective as thickeners, i.e., viscosifiers, for aqueous compositions. Typically, the amount of the polymer employed to achieve thickening efficiency, is from about 0.05 to about 5 weight percent based on the total weight of the composition. The specific amount of polymer will be dependent upon the particular end use and can be determined by those skilled in the art.

In addition, other ingredients, such as, for example, surfactants, preservatives, co-thickeners, such as, for example, polysaccharide ethers, solvents and other materials known to those skilled in the art can be employed in the compositions of the present invention.

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The polymers described herein are useful in a variety of aqueous systems, such as textile coatings (woven and nonwoven), latex paint formulations, cosmetic formulations, pigment dispersions and slurries, dentrifrices, hand lotions, liquid detergents, quenchants, agricultural chemicals, concrete additives, transmission fluids, waste water treatment (flocculants), turbulent drag reduction, automation coatings (OEM and refinish), architectural coatings, industrial coatings and the like. Other applications include, for example, paper making, mineral processing, brine viscosification, superabsorbency, enhanced oil recovery, personal care products, biomedical, pharmaceutical and the like.

The polymers of the present invention are particularly suitable for use in personal care compositions, e.g., hair care compositions and skin care compositions. Typical personal care compositions comprise the polymer of the present invention, water and a suitable personal care ingredient.

As used herein, the term "personal care ingredient" includes, but is not limited to, active ingredients, such as, for example, spermicides, virucides, analgesics, anesthetics, antibiotic agents, antibacterial agents, antiseptic agents, vitamins, corticosteroids, antifungal agents, vasodilators, hormones, antihistamines, autacoids, kerolytic agents, anti-diarrhea agents, anti-alopecia agents, anti-inflammatory agents, glaucoma agents, dry-eye compositions, wound healing agents, exfoliating agents, sunscreens, anti-oxidants, enzymes, anti-infection agents, and the like, as well as solvents, diluents and adjuvants such as, for example, water, ethyl alcohol, isopropyl

alcohol, higher alcohols, glycerine, propylene glycol, sorbitol, preservatives, surfactants, menthol, eucalyptus oil, other essential oils, fragrances, viscosity adjusters, polymers other than those of the present invention, and the like.

Such other polymers include, for example, naturally occurring and synthetic neutral, cationic, anionic and amphoteric polymers, e.g., polysaccharide ethers, hyaluronic acid, polyalkylene oxides and polycarboxylic acids. The polysaccharides include naturally occurring, biosynthesized and derivatized carbohydrate polymers or mixtures thereof. Such materials encompass high molecular weight polymers composed of monosaccharide units joined by glycosidic bonds. These materials may include, for example, the entire starch and cellulose families; pectin, chitosan; chitin; the seaweed products such as agar and carrageenan; alginate; the natural gums such as guar, arabic and tragacanth; bio-derived gums such as xanthan; and the like. Common polysaccharides include cellulose ethers, such as, for example, chemical cotton, cotton linters, wood pulp, alkali cellulose and the like. Such materials are commercially available. The molecular weight of the polysaccharides typically ranges from about 10,000 to 2,000,000 grams per gram mole.

Preferably, the polysaccharides are etherified by reacting the polysaccharide with an alkylene oxide, e.g., ethylene oxide, propylene oxide or butylene oxide. The amount of ether substitution is typically from about 1.5 to 6 and preferably from about 2 to 4 moles of ether substituent per mole of polysaccharide

ether. The polysaccharide ethers may be substituted with one or more desired substituents, e.g., cationic, anionic and/or hydrophobic substituents. Hydrophobic substituents are known in the art, examples of which are described above.

Hydrophobically-modified cellulose ethers are described, for example, in U.S. Patent Nos. 4,228,277, 5,120,328 and 5,504,123 and European Patent Publication 0 384 167 B1. Cationic, hydrophobically modified cellulose ethers are described, for example, in U.S. Patent No. 4,663,159. The substitution level of each such substituent on the polysaccharide ether is typically from about 0.001 to 0.1 and preferably from about 0.004 to about 0.05 moles of substituent per mole of polysaccharide ether.

Preferred polysaccharide ethers for use in accordance with the present invention, are cellulose ethers, including for example, hydroxyethyl cellulose, hydroxypropyl cellulose, methyl cellulose, ethyl cellulose, hydroxypropyl methyl cellulose, hydroxyethyl methyl cellulose, carboxymethyl cellulose, hydroxyethyl carboxylmethyl cellulose, and derivatives thereof.

Such personal care ingredients are commercially available, e.g., from Amerchol Corporation, Edison, NJ. Further details concerning the selection and amounts of such personal care ingredients are known to those skilled in the art.

Typical personal care compositions in accordance with the present invention may, for example, contain the following ingredients with the proportions listed below as weight percent active. The ingredients are listed as International Nomenclature of Cosmetic Ingredients ("INCI") names which can be found, for

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example, in the International Cosmetic Industrial Dictionary, 6th
Edition, Cosmetic Toiletries and Fragrances Association (1995).

TYPICAL FORMULATIONS**Mousse for skin conditioning****Ingredients:**

	%
Oleth-10	1.00
PPG-10 Methyl Glucose Ether	3.00
Deionized Water	q.s. 100
PEG 14M	0.10
Polymer of Invention	0.10
Aminomethylpropanol	q.s. pH=5.5
Preservatives	q.s.
SD Alcohol 40	15.00
A-46 Hydrocarbon propellant	4.00

Mousse for hair styling/conditioning**Ingredients:**

	%
Dimethicone Copolyol	1.00
PVP/VA Copolymer	2.00
Polyquaternium-24	0.30
Deionized Water	q.s. 100
Polymer of Invention	0.125
Aminomethylpropanol	q.s. pH=5.5
SD Alcohol 40	15.00
A-46 Hydrocarbon Propellant	4.00

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Styling Gel**Ingredients:**

	%
Deionized Water	q.s. 100
Polymer of Invention	1.25
PVP/VA Copolymer	4.00
Triethanolamine	q.s. pH=5.8
Methyl Gluceth-20	5.00
Preservatives	q.s.
Color	q.s.

Hand Lotion**Ingredients:**

	%
Mineral Oil	8.00
Cetyl Acetate/Acetylated Lanolin Alcohol	1.00
Glyceryl Stearate	0.50
Methyl Glucose Sesquistearate	3.00
PEG-20 Methyl-Glucose Sesquistearate	2.00
Dimethicone	0.50
Deionized water	q.s. 100
Methyl Gluceth-10	0.50
Polymer of Invention	0.20
Preservatives	q.s. 100
Triethanolamine	q.s. pH = 7.0

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Spray Gel**Ingredients:**

	%
Deionized water	q.s. 100
Polymer of Invention	0.30
Methyl Gluceth-20	4.00
Dimethicone Copolyol	2.00
Triethanolamine	q.s. pH = 5.8
PVP/VA Copolymer	5.00

Curl Activator**Ingredients:**

	%
Deionized water	q.s. 100
Polymer of Invention	0.50
Glycerine	10.00
Propylene Glycol	5.00
Methyl Gluceth-10	5.00
Preservative	q.s.
Triethanolamine	q.s. pH = 6.0

Shampoo**Ingredients:**

	%
Deionized water	q.s. 100
Ammonium Laureth Sulfate	10.00
Ammonium Lauryl Sulfate	5.00
Cocamide MEA	3.00
Coco-Betaine	1.00
Polymer of Invention	1.0
Dimethicone	1.00
Deionized Water	10.00
Polyquaterinium-10	0.30
Triethanolamine	q.s. pH = 6.5
Preservatives	q.s.

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Cream Rinse**Ingredients:**

	%
Cetearyl Alcohol (and) Cetareth-20	4.00
Cetyl Alcohol	1.00
Polysorbate 80	0.50
Deionized Water	q.s. 100
Polymer of Invention	0.50
Triethanolamine	q.s. pH =6.0
Lauryl Methyl Gluceth-10	1.00
Hydroxypropyldimonium Chloride	
Preservatives	q.s.

The invention is hereinafter described with reference to the Examples which are not intended to limit the claims which follow.

The following Example is illustrative of the preparation of the nonionic urethane monomers of this invention.

EXAMPLE 1**(Preparation of a Urethane Monomer)**

To a one-liter glass reactor fitted with a thermometer, heating mantle, thermoregulator, stirrer, nitrogen sparge, and condenser including a Dean-Stark trap is charged 800.0 g of a 40 mole ethoxylate of behenyl alcohol as a hot melt. The reactor contents are heated, with nitrogen sparging, to 110° C. and held for two hours while trace moisture is removed and collected in the Dean-Stark Trap (typically less than 1 g).

The reactor contents are then cooled to 80° C., the Dean Stark trap is replaced with a condenser, and the nitrogen sparge is switched to an air sparge for 15 minutes. With continued air sparging, 0.02 g methoxyhydroquinone inhibitor, 0.50 g dibutyl tin dilaurate catalyst, and 81.0 g of alpha, alpha-dimethyl-m-isopropenyl benzyl isocyanate (m-TMI, a

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product of Cytec Industries, Inc. Stamford, CT, may be used) are charged in order to the reactor. After a rapid initial exotherm which increases the reaction temperature about 80 C., the contents are heated to maintain 80o C. for an additional two hours. The product is then cooled to room temperature.

The final product is a white wax in appearance with residual isocyanate content of less than 0.5% and with 98% of the original ethylenic unsaturation retained.

EXAMPLE 2

(Preparation of an Alkali-Soluble Thickener with Urethane Monomer)

To a three-liter flask equipped with thermometer, stirrer, condenser, nitrogen inlet, thermoregulated water bath and monomer addition pump is charged 989.0 g deionized water and 4.0 g of 2-sulfoethyl methacrylate. The water is heated to 80o C. and purged with nitrogen for 30 minutes.

A pre-mix of monomers is prepared in a separate stirred container by charging, in order, 171.0 g methacrylic acid, 203.0 g methyl acrylate, 21.0 g dioctyl sodium sulfosuccinate, Triton GR-9M surfactant, a product of Union Carbide Corporation (sodium lauryl sulfate may be used as an alternative) and 56.0 g of the ethoxylated urethane monomer prepared in Example 1.

Under a nitrogen blanket, 45.0 g (10%) of the monomer pre-mix is charged to the reactor followed by 36 g of 1% sodium persulfate, 3% sodium bicarbonate solution. The contents exotherm to about 85o C., and after cooling back to 80o C. The addition of the remaining pre-mix is started and continued progressively over 2.5 hours until complete. The reactor contents are heated for an additional 30 minutes at 80o C. to

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complete the conversion of monomer to copolymer and then cooled to 60 C, at which point 2.0 g of a 6 wt% solution of t-butyl hydroperoxide is added followed by 2.0 g of a 6 wt% solution of isoascorbic acid added over 15 minutes to scavenge residual monomer to below 2 ppmw.

The product is a low viscosity latex of solids content 25.1%, RVT Brookfield viscosity 19 cps (No. 1 spindle at 100 rpm), pH of 2.5, and average particle size of 92 nanometers ("nm").

Example 3 Control

Preparation of Alkali Soluble Thickener having Ethyl Group with Urethane Monomer

A polymer is prepared in accordance with the procedure set forth in Example 2 with the exception that ethyl acrylate is substituted for the methyl acrylate referred to in Example 2.

The product is a low viscosity latex of solids content 25.0%, RVT Brookfield viscosity 19 cps (No. 1 spindle at 100 rpm), pH of 2.6, and average particle size of 92 nm.

Example 4

Viscosity Dependence on pH

The polymers prepared in Examples 2 and 3 were treated with various amounts of an alkaline material, e.g., 10% NaOH and the viscosity was measured as a function of pH. The viscosity was measured using a Brookfield LVT DV-II Viscometer with a # 3 spindle at a concentration of 1.00 weight percent polymer at 20°C and a speed of 12 rpm.

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The results are shown in Table 2 below.

TABLE 2
pH Dependence

	<u>Example 2</u>	<u>Example 3 (control)</u>
pH	Viscosity, cP	Viscosity, cP
4	1	1
4.5	1	1
5.0	1,000	1
5.5	35,000	1
6.0	75,000	1
6.5	80,000	60,000
7.0	85,000	80,000

It can be seen from the data presented in Table 1 that quite surprisingly, the replacement of ethyl acrylate with methyl acrylate in the polymer of the present invention resulted in a substantial reduction in the pH necessary to achieve viscosification of the aqueous composition.

Although the present invention has been described with respect to specific aspects, those skilled in the art will recognize that other aspects are intended to be included within the scope of the claims which follow.

It is Claimed

1. A polymer comprising the reaction product of:
 - (A) an unsaturated carboxylic acid monomer;
 - (B) a monoethylenically unsaturated monomer different from monomer (A); and
 - (C) a macromonomer comprising a hydrophobic portion and an alkoxyated portion which is polymerizable with monomer (A) and monomer (B);characterized in that:
 - (i) the monoethylenically unsaturated monomer (B) comprises a methyl group; and
 - (ii) the polymer has a viscosity of at least 10,000 cP at a pH of less than about 6.0.
2. The polymer of claim 1 wherein the hydrophobic macromonomer is a urethane monomer comprising the reaction product of a monohydric surfactant and a monoethylenically unsaturated isocyanate.
3. The polymer of claim 1 wherein monomer (B) is an acrylate.
4. The polymer of claim 3 wherein monomer (B) is methyl acrylate.

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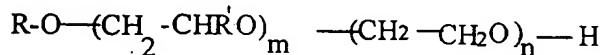
5. The polymer of claim 1 which comprises from about 20 to 80 weight percent of monomer (B) based on the total weight of the polymer.

6. The polymer of claim 1 wherein the unsaturated carboxylic acid monomer is selected from the group consisting of acrylic acid, methacrylic acid, crotonic acid itaconic acid and mixtures thereof.

7. The polymer of claim 1 which comprises from about 20 to 70 weight percent of monomer (A) based on the total weight of the polymer.

8. The polymer of claim 2 wherein the monohydric surfactant is an alkoxyated aliphatic alcohol or alkyl phenol.

9. The polymer of claim 8 in which said monohydric surfactant has the formula:



in which R is an alkyl group containing 6-30 carbon atoms or an alkaryl group containing 8-30 carbon atoms, R' is C1-C4 alkyl, n is an average number from about 6-150, and m is an average number of from 0-50 provided n is at least as great as m and $n + m = 6-150$.

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10. A polymer of claim 2 in which said monomer (C) is a urethane reaction product of said monohydric surfactant with alpha, alpha-dimethyl-m-isopropenyl benzyl isocyanate.
11. The polymer of claim 1 wherein the hydrophobic portion of the macromonomer is an aliphatic alcohol of a vegetable origin.
12. The polymer of claim 11 wherein the alcohol has from about 20 to 24 carbon atoms.
13. The polymer of claim 12 wherein the alcohol is behenyl alcohol.
14. The polymer of claim 1 which comprises from about 0.5 to 60 weight percent of monomer (C) based on the total weight of the polymer.
15. The polymer of claim 1 comprising from about 35 to 45 weight percent of monomer (A), from about 45 to 55 weight percent of monomer (B) and from about 5 to 15 weight percent of monomer (C) based on the total weight of the polymer.
16. A composition comprising the polymer of claim 1 and water.
17. The composition of claim 16 further comprising at least one personal care ingredient.

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18. The composition of claim 16 having a viscosity of at least 20,000 cP at a pH of less than about 6.0.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 99/13406

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C08F220/04 A61K7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 382 641 A (K. KAWATE) 17 January 1995 (1995-01-17) claim 1 ---	1
A	US 4 916 183 A (M. BARRON) 10 April 1990 (1990-04-10) ---	
A	DE 37 35 141 A (CESKOSLOVENSKA AKAD. VED.) 21 April 1988 (1988-04-21) ---	
A	WO 95 00565 A (UNION CARBIDE CHEMICALS & PLASTICS) 5 January 1995 (1995-01-05) cited in the application ---	
A	US 4 514 552 A (G. SHAY) 30 April 1985 (1985-04-30) cited in the application ---	
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

24 September 1999

Date of mailing of the international search report

01/10/1999

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/13406

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 350 414 A (SOC. COATEX) 10 January 1990 (1990-01-10) -----</p>	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PC1/US 99/13406

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5382641 A	17-01-1995	JP 6127151 A	10-05-1994
US 4916183 A	10-04-1990	US 5013787 A	07-05-1991
		US 5011978 A	30-04-1991
		CA 1297124 A	10-03-1992
DE 3735141 A	21-04-1988	CS 8607492 A	16-09-1988
		AT 272387 A	15-11-1991
		FR 2605324 A	22-04-1988
		GB 2198442 A, B	15-06-1988
WO 9500565 A	05-01-1995	US 5399618 A	21-03-1995
		AT 154812 T	15-07-1997
		AU 702693 B	04-03-1999
		AU 7315294 A	17-01-1995
		CA 2166195 A	05-01-1995
		DE 69403967 D	31-07-1997
		DE 69403967 T	20-11-1997
		EP 0706535 A	17-04-1996
		ES 2105737 T	16-10-1997
		FI 956274 A	27-02-1996
		JP 8512064 T	17-12-1996
		NO 955315 A	20-02-1996
		PL 307744 A	12-06-1995
		US 5436292 A	25-07-1995
		US 5476900 A	19-12-1995
		US 5561189 A	01-10-1996
		US 5629375 A	13-05-1997
US 4514552 A	30-04-1985	AU 573021 B	26-05-1988
		AU 4613685 A	27-02-1986
		CA 1278893 A	08-01-1991
		EP 0173109 A	05-03-1986
		JP 1943616 C	23-06-1995
		JP 6078412 B	05-10-1994
		JP 61060719 A	28-03-1986
		NZ 213201 A	28-07-1988
		PT 80946 A, B	01-09-1985
		US RE33156 E	30-01-1990
EP 350414 A	10-01-1990	FR 2633930 A	12-01-1990
		AT 75234 T	15-05-1992
		AU 612275 B	04-07-1991
		AU 3788489 A	11-01-1990
		CA 1334776 A	14-03-1995
		DK 335289 A	08-01-1990
		FI 893310 A, B,	08-01-1990
		GR 3004447 T	31-03-1993
		JP 2099573 A	11-04-1990
		PT 91085 A, B,	08-02-1990
		US 5015711 A	14-05-1991
		US 5066710 A	19-11-1991